

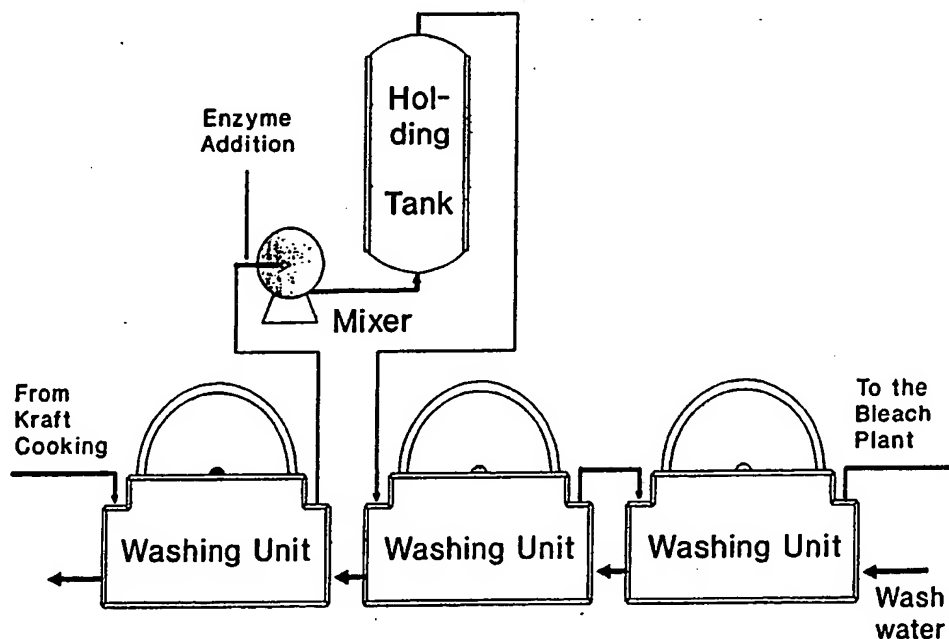


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2034/90 24 August 1990 (24.08.90) DK(71) Applicant (for all designated States except US): **NOVO NORDISK A/S [DK/DK]; Novo Allé, DK-2880 Bagsvaerd (DK).**

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With international search report.(54) Title: **PROCESS FOR TREATMENT OF LIGNOCELLULOSIC PULP AND APPARATUS FOR PERFORMANCE OF THE PROCESS**

(57) Abstract

A process for treatment of lignocellulosic pulp comprising a multistage washing of the unbleached kraft brown stock and a xylanase treatment. The xylanase treatment is carried out in a holding tank introduced upstream the first washing unit or downstream one or more of the other washing units except for the last washing unit.

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PROCESS FOR TREATMENT OF LIGNOCELLULOSIC PULP AND APPARATUS FOR PERFORMANCE OF THE PROCESS

A common stage in the treatment of wood chips for paper production is chemical pulping, e.g. the so-called kraft process which is an alkaline sulphate cooking of the wood chips. The native wood chips contain around 30% lignin, and at the end of the chemical cooking process less than 5% of the lignin compounds is still left in the pulp. Due to the strong brown color of the remaining lignin and its tendency to darken in UV light or by oxidation this has to be removed in order to obtain a white pulp without the tendency to color reversion.

10 After the sulphate cooking a multistage washing of the unbleached kraft brown stock takes place. The well washed brown stock can then be treated with an enzyme preparation followed by a subsequent wash before entering the bleach plant.

The invention comprises an improvement of this conventional multistage washing of the unbleached kraft brown stock, followed by the enzyme treatment with the subsequent wash, whereby this improvement is a modification, which improves the economy and facilitates the processing.

After a multistage washing of the unbleached kraft brown stock followed by an enzyme treatment with the subsequent wash the brown color can be removed by a multistage bleaching using e.g. chlorine and/or chlorine dioxide. Due to the ever increasing environmental concern, the dosage of chlorine and/or chlorine dioxide has to be kept at a minimum, and it is for that reason that the enzymatic treatment of the kraft cooked pulp has been introduced, vide e.g. The third International Conference on Biotechnology in the Pulp and Paper Industry, 25 Stockholm, 16-19.6, 1986, page 67-69.

Thus, the sequence of the prior art processes in regard to paper pulping is the following:

- 1) kraft cooking of the wood chips,
- 2) multistage washing of the unbleached kraft brown stock
- 30 3) enzymatic treatment of the washed brown stock
- 4) bleaching.

The invention comprises the above indicated processes 2) and 3) and is an improvement thereof, as explained in more detail in the following.

Hitherto the multistage washing of the unbleached kraft brown stock has been performed as indicated on the flow sheet of Fig. 1. In addition to the 5 process stages indicated on Fig. 1 an oxygen delignification stage with subsequent washing may be included either before or after the enzyme stage. This prior art process with an enzyme treatment introduced between the cooking and the bleaching sections has some serious drawbacks, e.g. (1) the enzyme stage includes a washing stage, which is a unit operation that represents a large 10 capital investment, and (2) pH adjustment of the pulp may be needed if enzymes with acid pH optimum are used.

Thus, the purpose of the invention is the provision of a process for treatment of lignocellulosic pulp which requires a less expensive apparatus or stated otherwise the provision of a reduction of the price of the prior art method 15 for treatment of lignocellulosic pulp comprising a multistage washing of the unbleached brown kraft stock with subsequent enzyme treatment, washing and bleaching, and a corresponding apparatus for performance of the process.

Now, according to the invention it has been found that the purpose of the invention can be fulfilled, if the enzymatic treatment with the subsequent wash 20 is abandoned altogether and the enzymatic treatment is introduced after one or more of the single washing units in the multistage washings of the unbleached kraft brown stock, or stated otherwise if the enzyme treatment is introduced upstream the prior art position of the enzyme treatment in the multistage washing, in such manner that the multistage washing for washing out of impurities from the 25 kraft cooking and washing out of the residues from the enzyme treatment is combined.

Thus, the process for treatment of lignocellulosic pulp according to the invention comprising a multistage washing of the unbleached kraft brown stock and a xylanase treatment is characterized by the fact that the xylanase 30 treatment is introduced upstream the prior art position of the xylanase treatment in such manner that the stock from the kraft cooking or the washed stock from the outlet side of one or more of the washing units is transported to a holding

4 tank, that a xylanase with high pH activity and stability and high heat stability is added directly upstream the holding tank, and that the enzyme treated stock is passed further on in the process to the next washing unit. Also in relation to the process according to the invention (Fig. 2) another non-chlorine bleaching stage, 5 e.g. an oxygen delignification stage or an ozone stage may be included either before or after the enzyme stage.

By comparison of Fig. 1 (prior art) and Fig. 2 (invention) it clearly appears that the invention requires one washing unit less than the prior art process, and thus, the process according to the invention fulfils the purpose of 10 the invention. Furthermore, as the tank on Fig. 1 used for the enzyme treatment normally also serves as buffer tank between the kraft cooking and the bleaching plant the residence time of the pulp in the tank often varies within a wide range, e.g. between 30 minutes and 24 hours. In the invention the tank is an integrated part of the washing process. It only serves the need for holding time for the 15 enzyme treatment, which makes it much easier to control the enzyme treatment time. Finally, the invention provides a much better connection to the existing wash water streams. The entire amount of wash water obtained in the process according to the invention will end up in the recovery system for the kraft cooking process, which means that everything that is solubilized during the enzyme 20 treatment will be burned in the recovery boiler whereby the BOD₅ load from the enzyme stage on the effluent streams is eliminated. This is not the case in the prior art system. In the prior art system the wash water from the washing stage after the enzyme treatment normally has to be sewered. The enzyme treatment according to the invention also releases more cooking chemicals from the pulp 25 than a conventional wash with water. This makes it possible to obtain an even better recovery of cooking chemicals than normally obtained.

The three washing units on Fig. 2 are not limiting to the invention, but just an example. Each single unit can represent more than one washing stage. With three washing units one, two or three enzyme treatment units can be 30 introduced according to the invention; just one enzyme treatment unit is shown on Fig. 2.

The xylanase with high pH activity and stability and with high heat stability, which is used in the process according to the invention, has to show a bleach boosting effect under the conditions present just prior to the last washing unit.

5 The bleach boosting effect is measured as the kappa number reduction of pulp after an enzyme treatment followed by a C/D-E bleaching compared to a control which is treated in the same way but without addition of enzyme: (Bleach boosting Effect = Kappa number after C/D-E bleaching of enzyme treated pulp minus kappa number after C/D-E bleaching of pulp treated
10 without enzyme).

Also, the invention comprises an apparatus for performance of the process according to the invention. The apparatus according to the invention is characterized by the fact that a holding tank with piping with facilities for introduction of enzyme is introduced upstream the first washing unit or
15 downstream one or more of the other washing units except for the last washing unit, that piping is provided for further transport of the stock to the next washing unit, and that the conventional enzyme treatment unit downstream the washing unit is abandoned.

It is to be understood that at least one holding tank with accessories
20 is introduced, and that the maximum number of holding tanks with accessories, which can be introduced into the sequence according to the invention equals the number of washing units in the multistage washing process.

The following example illustrates the invention in comparison to prior art.

25 EXAMPLE 1

In order to illustrate the invention an unbleached and unwashed softwood pulp identified as P was washed in one stage as follows:

The pulp P was diluted with fresh water to a consistency of 1% DS and then reconcentrated to a consistency of approximately 20% on a wire screen.

This washing sequence is the standard washing stage used throughout this example.

After the washing the pH of the pulp was 9.7.

This pulp sample was divided into two halves.

5 The first half of this one stage washed pulp was xylanase treated under the following conditions without pH adjustment prior to the enzyme addition.

Temperature	:	70°C
pH	:	9.7
10 Consistency	:	10%
Time	:	3 hours
Xylanase	:	<i>Streptomyces olivochromogenes</i> , vide Example 6 in WO 91/02839
Enzyme dosage	:	5000 EXU/kg dry pulp

15 The definition of the EXU xylanase activity unit appears from AF 293.9/1, obtainable on request from NOVO NORDISK A/S, Novo Allé, DK-2880 Bagsvaerd, Denmark.

The xylanase stage was carried out as follows. The pulp was diluted to the desired consistency by addition of fresh water. The enzyme solution was 20 added and mixed into the pulp by vigorous mixing. The pulp was then placed in a water bath to ensure constant temperature for the remainder of the treatment time. The pulp was not mixed during the three hours of holding time.

After the enzyme stage the pulp was carried through two standard washing stages. This pulp sample which was enzyme treated between the first 25 and the second washing stage, was carried out according to the invention and will be referred to later as inv 1-2.

The second half of the one stage washed pulp was carried through another standard washing stage. After washing the pH of the pulp suspension was 8.7.

This two stage washed pulp was enzyme treated without pH adjustment prior to the enzyme addition under the following conditions:

	Temperature	:	70°C	
	pH	:	8.7	
5	Consistency	:	10%	
	Time	:	3 hours	
	Enzyme	:	<i>Streptomyces olivochromogenes</i> , vide Example 6 in WO 91/02839	
	Enzyme dosage	:	2000 EXU/kg dry pulp	

10 The enzyme treatment was carried out as described above.

After the enzyme stage the pulp was carried through one standard washing stage. This sample of pulp, which was enzyme treated between the second and third washing stage, was carried out according to the invention and will be referred to later as inv 2-3.

15 In order to illustrate the corresponding prior art the pulp P was first carried through three standard washing stages. Then the pH of the pulp was lowered to 6.5 by addition of sulfuric acid and an enzyme stage was carried out under the following conditions.

20	Temperature	:	50°C
	pH	:	6.5
	Consistency	:	10%
	Time	:	3 hours
	Enzyme	:	Pulpzyme™HA
	Enzyme dosage	:	275 FXU/kg dry pulp

25 The definition of FXU xylanase activity unit appears from AF 293.6/1,
obtainable on request from NOVO NORDISK A/S, Novo Allé, DK-2880 Bagsvaerd,
Denmark.

The enzyme treatment was made as described above.

After the enzyme stage the pulp was washed in an extra standard washing stage according to the prior art. This pulp sample will be referred to later as prior.

The above experiment used to illustrate prior art was repeated except that no enzyme was added. This experiment served as a control to demonstrate that the enzyme stage really has an effect on the pulp and will be referred to later as control.

The xylanases used in this example were selected according to their pH optimum in relation to the pH of the pulp.

After enzyme treatments and washings all the pulps were bleached according to the same two stage bleaching sequence (D50 C50) E.

The bleachings were carried out under the following conditions:

(D50 C50):

15	Temperature	:	50°C
	Consistency	:	5%
	Time	:	20 minutes
	active Cl dosage	:	5.7% (w/w) on dry pulp

E:

20	Temperature	:	60°C
	Consistency	:	10%
	Time	:	1 hour
	NaOH dosage	:	4.2% (w/w) on dry pulp

After the bleaching the kappa number of all four pulps were determined.

Results

Kappa number of the pulps after the (D50 C50) E bleachings:

	Kappa number	delta Kappa number %
5 Control	2.85	-
Prior	2.52	11.6
inv 1-2	2.50	12.3
inv 2-3	2.31	19.0

It is observed that the kappa number of the enzyme treated pulps are reduced compared to the control. This demonstrates that the enzyme treatment in all three sequences, the prior art and the two inventive sequences, has shown a bleach boosting effect.

It is also seen that the kappa numbers obtained by the two sequences carried out according to the invention are lower than the kappa numbers for the prior art sequence.

This demonstrates that the sequence described by the invention besides giving the technical advantages of avoiding one washing unit gives just as good a kappa number reduction or even a better kappa number reduction as the prior art sequence.

CLAIMS

1. Process for treatment of lignocellulosic pulp comprising a multistage washing of the unbleached kraft brown stock and a xylanase treatment, characterized by the fact that the xylanase treatment is introduced upstream the
5 prior art position of the xylanase treatment in such manner that the stock from the kraft cooking or the washed stock from the outlet side of one or more of the washing units is transported to a holding tank, that a xylanase with high pH activity and stability and high heat stability is added directly upstream the holding tank, and that the enzyme treated stock is passed further on in the process to
10 the next washing unit.
2. Apparatus for performance of the process according to Claim 1, characterized by the fact that a holding tank with piping with facilities for introduction of enzyme is introduced upstream the first washing unit or
15 downstream one or more of the other washing units except for the last washing unit, that piping is provided for further transport of the stock to the next washing tank, and that the conventional enzyme treatment unit downstream the washing unit is abandoned.

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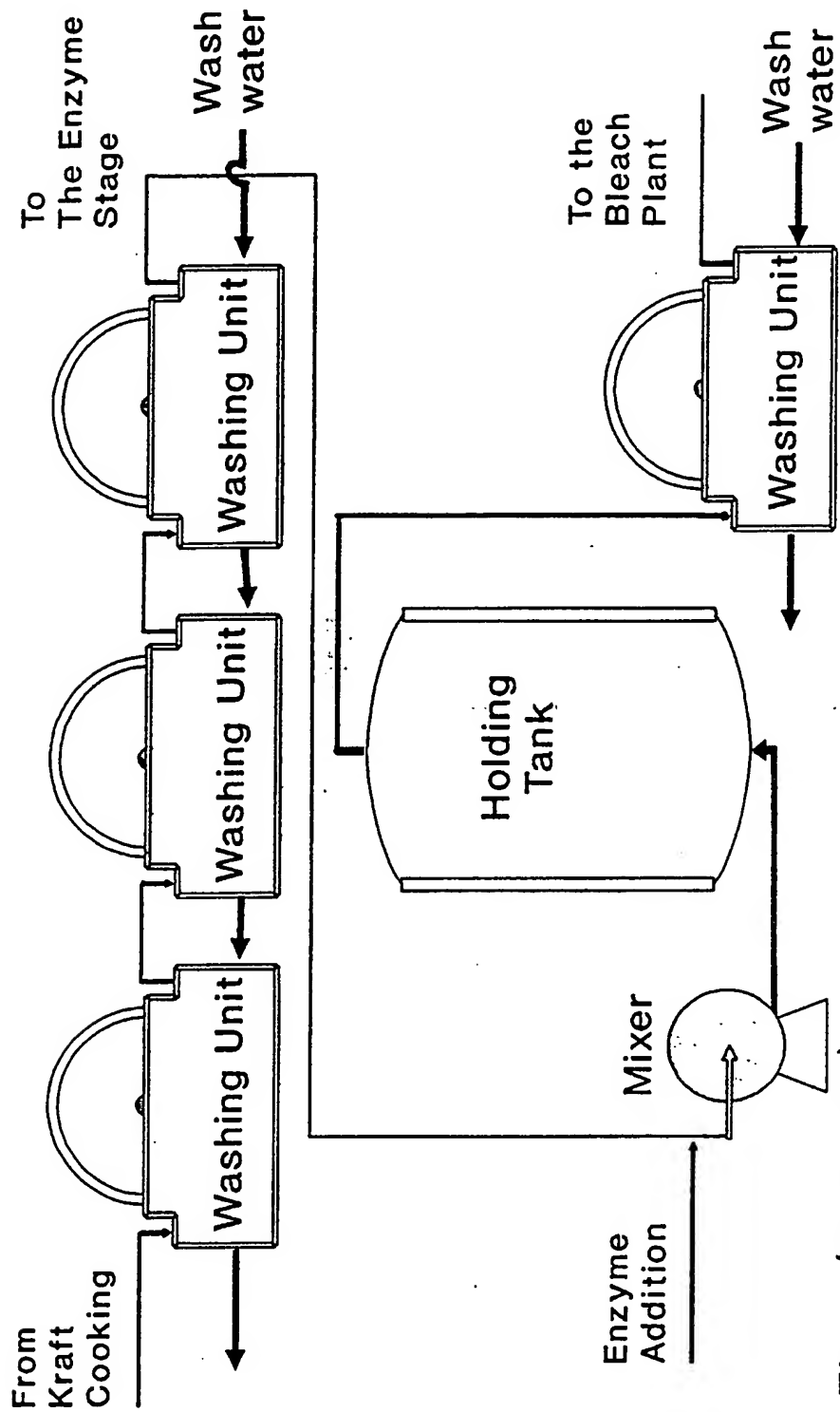


Fig. 1 (Prior Art)

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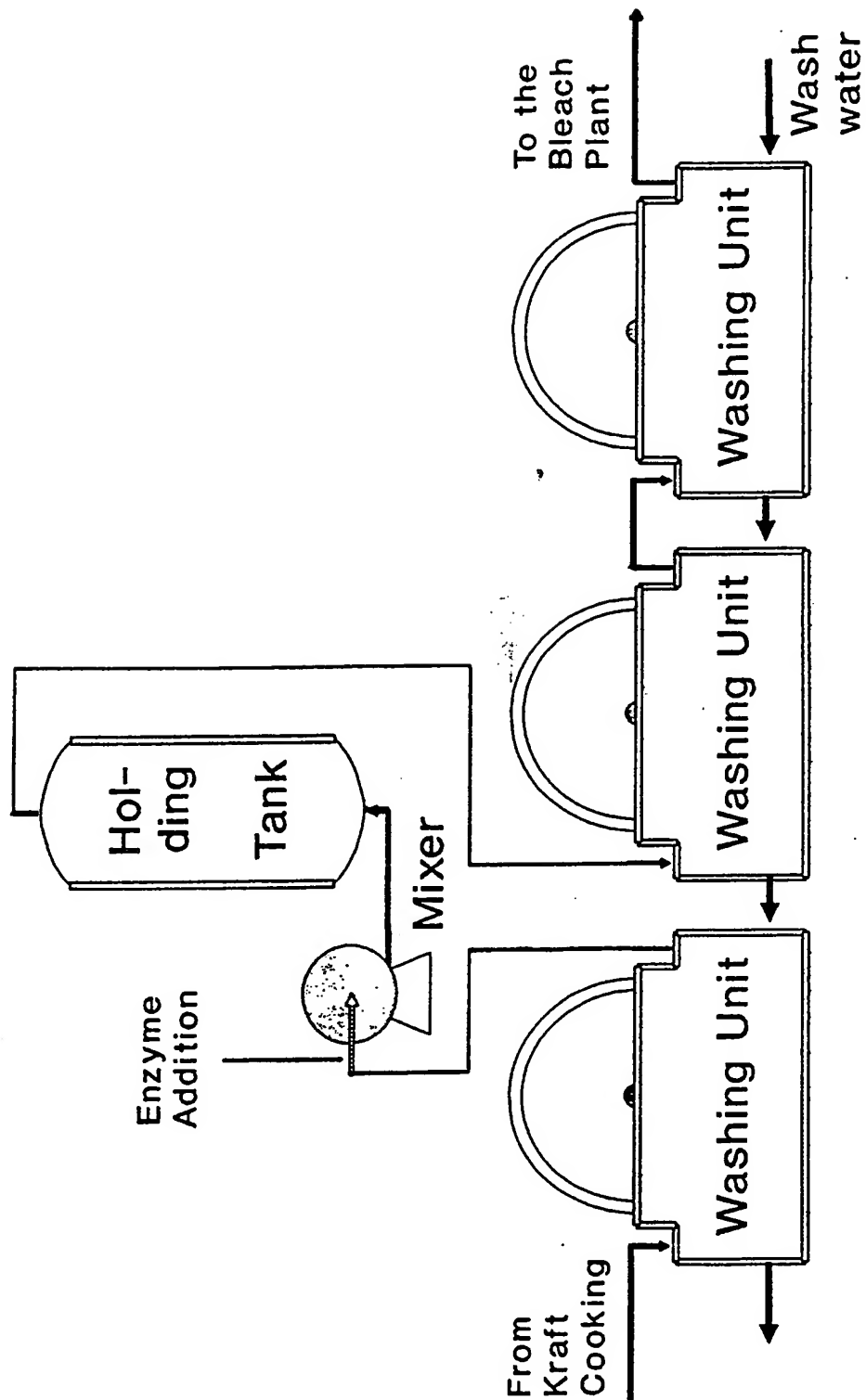


Fig. 2 (The invention)

INTERNATIONAL SEARCH REPORT

International Application No. **T/DK 91/00239**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁸ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: D 21 C 9/02, 9/10																	
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">IPC5</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">D 21 C</td> </tr> </table> <div style="text-align: center; border: 1px solid black; padding: 2px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p style="padding: 5px;">SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	D 21 C											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 2px;">Category *</th> <th style="width: 60%; padding: 2px;">Citation of Document,¹¹ with Indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; padding: 2px;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP, A2, 0383999 (ENSO-GUTZEIT OY) 29 August 1990, see page 1, line 39 - line 43</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td style="text-align: center; vertical-align: top; padding: 5px;">2</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP, A2, 0373107 (SANDOZ AG) 13 June 1990, see page 6, line 40 - line 47</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td style="text-align: center; vertical-align: top; padding: 5px;">2</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	EP, A2, 0383999 (ENSO-GUTZEIT OY) 29 August 1990, see page 1, line 39 - line 43	1	A	--	2	X	EP, A2, 0373107 (SANDOZ AG) 13 June 1990, see page 6, line 40 - line 47	1	A	--	2
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 29th November 1991 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 1991 -12- 06 </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> Marianne Bratsberg </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 29th November 1991	Date of Mailing of this International Search Report 1991 -12- 06	International Searching Authority <div style="text-align: center; margin-top: 10px;">SWEDISH PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> Marianne Bratsberg </div>											
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ON INTERNATIONAL PATENT APPLICATION NO. PCT/DK 91/00239

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The members are as contained in the Swedish Patent Office EDP file on 31/10/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0383999	90-08-29	JP-A- 2221482	90-09-04
EP-A2- 0373107	90-06-13	CA-A- 2003503	90-05-23
		JP-A- 2210085	90-08-21

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